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New Low Thermal Conductivity Materials for Thermoelectric Applications

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Abstract

A low lattice thermal conductivity is one of the requirements to achieve high thermoelectric figures of merit. Several low thermal conductivity materials were identified and developed over the past few years at JPL, including filled skutterudites and Zn_4Sb_3-based materials. A study of the mechanisms responsible for the high phonon scattering rates in these compounds has demonstrated that materials with highly disordered or complex structures which can accommodate additional atoms in their lattice are likely to have low lattice thermal conductivity values. Several cluster compounds, including the Chevrel phases (Mo_6Se_8-type) and Re_6Te_{15}, are just such materials and are currently being investigated at JPL. The crystal structures of the Chevrel phases present cavities which can greatly vary in size and can contain a large variety of atoms ranging from large ones such as Pb to small ones such as Cu. These atoms are not localized in the structure and, depending on their size, can move between different sites and may produce significant phonon scattering. Although most of the Chevrel phases studied until now were reported to be metallic, it was found that scmiconducting Chevrel phases can be engineered by controlling the number of electrons per [Mo_6] cluster. Initial results obtained on some cluster Chevrel phases and Re_6Te_{15} are presented and discussed. These materials possess very low thermal conductivity values (- 10 mW/cmK at 300K) but optimization of their electronic properties will be required to achieve high thermoelectric figures of merit.

Introduction

Renewed interest in the search for thermoelectric materials with superior properties has been driven by several factors. The availability and identification of new compounds and concepts as well as economical and environmental concerns have substantially contributed to the revival of the thermoelectric field. Several new ideas have been recently reviewed [1]. One of the new approaches is to look at materials which can be referred to as "rattling" semiconductors. The idea was originally proposed by Slack [2] who suggested that, in crystals containing loosely bound atoms, phonons should be scattered more strongly than electrons (holes). He called such an ideal thermoelectric material a "phonon-glass, electron-crystal"-(PGEC). Efforts to identify new classes of thermoelectric materials init iated at the Jet Propulsion laboratory (JPL) in 1991 have resulted in the discovery of several materials with superior thermoelectric properties, including skutterudites and ZtbSb~-based materials [3-5]. Studies on skutterudites initially focused on binary compounds but it became soon clear that thermoelectric figures of merit (ZT) greater than those obtained for state-of-the-art thermoelectric materials would not be achieved if the lattice thermal conductivity could not be significantly reduced. One of the features of the skutterudite compounds is the presence of voids in their crystal structure. These cavities can be filled by various atoms which are believed to produce an important phonon scattering, resulting in a significant reduction in lattice thermal conductivity and superior thermoelectric properties [5-8].

These findings support the concept initially proposed by Slack. Other crystalline materials containing loosely bound atoms have also been reported to posses thermal conductivity close to the calculated theoretical minimum [9]. We have conducted a search to identify new classes of materials with crystal structures that can host "rattling" atoms and to investigate their thermoelectric properties. We describe in this paper several cluster compounds which present such attributes: Chevrel phases and Re_6Te_{15}-based compounds recent experiments show that they possess very low thermal conductivity and a good potential for thermoelectric applications.

Chevrel phases

Structure and physical properties

Ternary chalcogenides of formula $M_xMo_6X_8$ (M= Cu, Ag, Ni, Fe, rare earth, etc.) and X = S, Se, or Te have been known since the 1970 's. They have attracted considerable interest because of their superconducting properties with large critical magnetic fields [10]. They were first synthesized by Chevrel et al. in 1971 [11] and therefore are often referred to as Chevrel compounds. The ternary phases have structures closely related to those of binary molybdenum chalcogenides Mo_6X_8 (X= S, Se, Te).

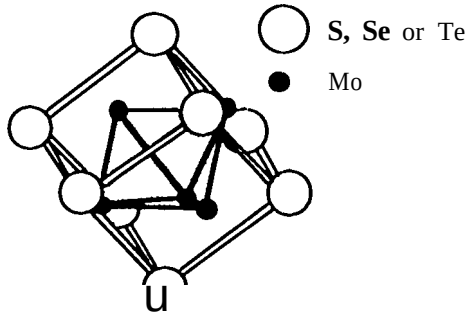

Figure 1: Illustration of the Mo_6X_8 (X - S, Se, Te) building block of the rhombohedral Chevrel phase structure.

The Mo_6X_8 unit is illustrated in Figure 1 and consists of an [Mo_6] octahedron "cluster" surrounded by eight chalcogens

arranged in a distorted cube. The rhombohedral Chevrel phase consists of a stacking of Mo_6X_8 units and contains channels where additional metal atoms can be inserted, forming MMo_6X_8 compounds where M can bc a variety of atoms from small to large ones (M– Ag, Sn, Ca, Sr, Pb, Ba, Ni, Co, Fe, Cr, Mn, . . . ; for a complete list see for example [12]). The cavities in the Chevrel structure arc empty in the binary compounds such as Mo_6Te_8 and are filled by the M atoms in the ternary compounds $M_xMo_6X_8$. The largest of the voids in the Chevrel structure has nearly a cubic shape formed by 8 chalcogen atoms as illustrated in Figure 2a. Large atoms such as Pb or La can exclusively occupy these large voids with a filling factor limit corresponding to x-1. Smaller atoms such as Cu, Ni or Fe, for example can be inserted in 12 different smaller holes with irregular shapes in the chalcogen channels as illustrated in Figure 2b. For small atoms, the upper occupancy limit was experimentally found to be corresponding to x=4. It is also important to point out that the shapes and sizes of the interstices depend on the composition and degree of filling. The thermal behavior of $M_xMo_6X_8$ compounds has been studied by Yvon [10]. One of the results of these studies is that it appears that the M atoms are systematically not confuted in a fixed position, are weakly bound and small atoms in particular are able to move between the 12 different lattice sites. The motion of these atoms within the lattice may be particularly effective in scattering. Data on thermal conductivity of $M_xMo_6X_8$ ternary compounds would therefore be of great interest.

As we mentioned above, these compounds have been mainly investigated for their superconducting properties. To the best of our knowledge, no data exists on the thermoelectric properties of Chevrel phases. Many of their physical properties appear to be linked to the number of electrons per Mo atom in the cluster. This quantity, often referred to as "cluster-valence-electron" (cluster-VEC) is calculated by adding the valence electrons of M atoms to the valence electrons of Mo atoms, by subtracting the number of electrons required to "fill" the octets of the chalcogen atoms and dividing the result by the number of Mo atoms [13]. Chevrel phases arc formed for cluster VEC numbers between 3.3 and 4. [13]. In addition, band structure calculations results predicted an energy gap in the electronic structure for 4 valence electrons pcr Mo atom in the cluster [14]. The "magic" number of 4 is met in the compound $Cu_4Mo_6S_8$ although the semiconducting nature of this compound was not confirmed experimentally. Values of 4 are also attained in mixed-rnctal cluster compounds such as $Mo_2Re_4Se_8$ and $Mo_4Ru_2Se_8$ [15, 16] and these compounds were found to be semiconductors, supporting the idea of an energy gap in the band structure of the Chevrel phases with a "magic" cluster VEC number of 4.

Wc have recently synthesized and investigated the thermoelectric properties of the compound $Mo_2Re_4Se_8$ [17], a pseudobinary compound with a VEC of 4. The results confirmed the expected semiconducting nature of this material. However, it was found that only very small amounts of an additional element M such as Sn can be introduced in the compound [15]. This might be explained by the fact that the cluster VEC is already at 4 and the bands below the gap are completely filled, preventing the insertion of additional M atoms. Other approaches must thus be considered to study the effect of void fillers on the thermal conductivity of

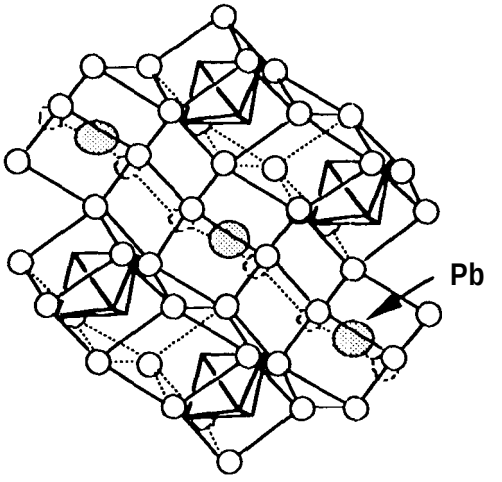

Figure 2a

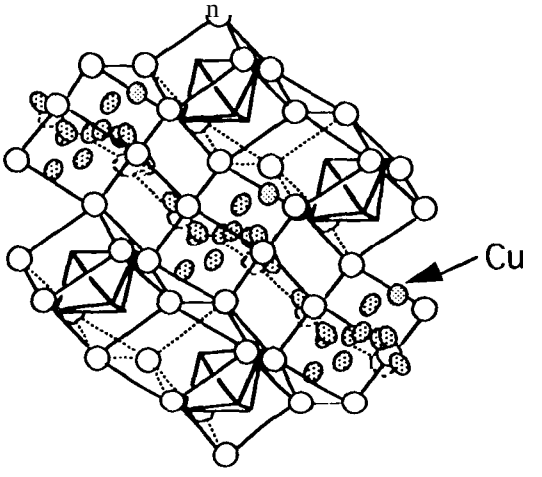

Figure 2b

Figure 2: Illustrations showing the positions of filling atoms in the cavities of the Chevrel crystal structure (after reference [10]). The figures represent a projection of the crystal structure on the hexagonal (1 120) plane. The large atoms of Pb in $PbMo_6S_8$ occupy cube shaped chalcogen holes (2a) whereas small Co atoms can be distributed over 12 different sites in the chalcogen network of $Cu_xMo_6S_8$ (x_{max}=4) (2 b).

semiconducting Chevrel phases, In the $Cu_xMo_6S_8$ system, compositions with x=4 have been reported [18] and, assuming that the Cu has an oxidation state of +1, the ionic formula would be $Cu_4^{+}Mo_6^{2+}S_8^{2-}$. The "magic" cluster VEC number of 4 is rnct in this compound which should be semiconducting. Another possibility to explore is to prepare semiconducting Chevrel phases combining void fillers and a mixed cluster ($Mo_{6-x}M'_x$, where M' is a metal) to achieve the "magic" VEC number of 4. For example, an hypothetical compound $Cu_2Mo_3Re_3Se_8$ would have a cluster VEC of 4 and should be a semiconductor. Such a compound would be particularly attractive because phonons would presumably be scattered by both point defects and the void tillers. Wc are currently

investigating some of these approaches and synthesized several $(Fe,Co)_xMo_6Se_8$ filled compositions. Assuming an oxidation state of 2+ for Fe and Co these compositions have a VEC of 4 for x–2 and therefore should be semiconducting. The details of the sample preparation, characterization and transport properties measurements as well as their thermoelectric properties are presented and discussed in the following sections.

Experimental

Single phase, polycrystalline samples of $(Fe,Co)_xMo_6Se_8$ were prepared by mixing and reacting stoichiometric amounts of iron (99.99%), cobalt (99.9990/.), molybdenum (99.999%), and selenium (99.999%) powders. The powders were first mixed in a plastic vial using a mixer before being loaded into quartz ampoules which were evacuated and sealed, The ampoules were then heated at 1473K for 2 days. A total of three anneals at 1473K for 2 days each and with intermediate crushing and grinding was necessary to obtain single phase materials. The samples were analyzed by x-ray diffractometry (XRD) after each anneal. The powders were then hot-pressed in graphite dies into dense samples, 10 mm long and 6.35 mm in diameter. The hot-pressing was conducted at a pressure of about 20,000 psi and at temperatures between 1123 and 1273 K for about 2 hours under argon atmosphere. The density of the samples was calculated from the measured weight and dimensions and was found to bc about 95°/0 of the theoretical density.

X-ray diffractometry analysis (XRD) was performed at room temperature on a Siemens D-500 diffractometer using Cu-K_α radiation, Small additions of Si powders were made to the samples as an internal standard. Powder x-ray patterns were taken with scan steps of 2Θ=0.05° and counting time of 3 s. Microprobe analysis (MPA) was performed on these samples to determine their atomic composition using a JEOL JXA-733 electron super-probe operating at 20x 10^3 Volts (V) of accelerating potential and 25x 10-9 Amperes (A) of probe current. Pure elements were used as standards and x-ray intensity measurements of peak and background were conducted by wavelength dispersive spectrometry. The shear and longitudinal sound velocities were measured at room temperature on a sample about 8 mm long using a frequency of 5 Mhz.

Samples in the form of disks (typically a 1.0 mm thick, 6.35 mm diameter slice) were cut from the cylinders using a diamond saw (perpendicular to the pressing direction) for electrical and thermal transport property measurements. All samples were. characterized at room temperature by Seebeck coefficient, Hall effect and electrical resistivity measurements. High temperature resistivity, Hall effect, Seebeck coefficient, thermal diffusivity, and heat capacity measurements were also conducted on selected samples between room temperature and about 1000K. The electrical resistivity (p) was measured using the van dcr Paw technique with a current of 100 mA using a special high temperature apparatus [19]. The Hall coefficient (R_H) was measured in the same apparatus with a constant magnetic field value of - 10,400 Gauss. The carrier density was calculated from the Hall coefficient, assuming a scattering factor of 1.0 in a single carrier scheme, by $p/n = 1/R_He$, where p and n are the densities of holes and electrons, respectively, and e is the electron charge. The Hall mobility (μ_H) was calculated from the Hall coefficient and the resistivity values by $\mu_H = R_H/\rho$. Errors were estimated to be ± 0.5°/0 and ± 2% for the resistivity and Hall coefficient data, respectively. The Seebeck coefficient (α) of the samples was measured on the same samples used for electrical resistivity and Hall coefficient measurements using a high temperature light pulse technique [20]. The error of the Seebeck coefficient measurement was estimated to be less than ±3%. The heat capacity and thermal diffusivity were measured using a flash diffusivity technique [21]. The thermal conductivity (λ) was calculated from the experimental density, heat capacity, and thermal diffusivity values. The overall error in the thermal conductivity measurements was estimated to be about ± 10O/O.

Results and discussion

The electrical resistivity and Seebeck coefficient values for Mo_6Se_8, $Mo_2Re_4Se_8$ and $(Fe,Co)_xMo_6Se_8$ Chevrel phases are shown in Figures 3 and 4, respectively.

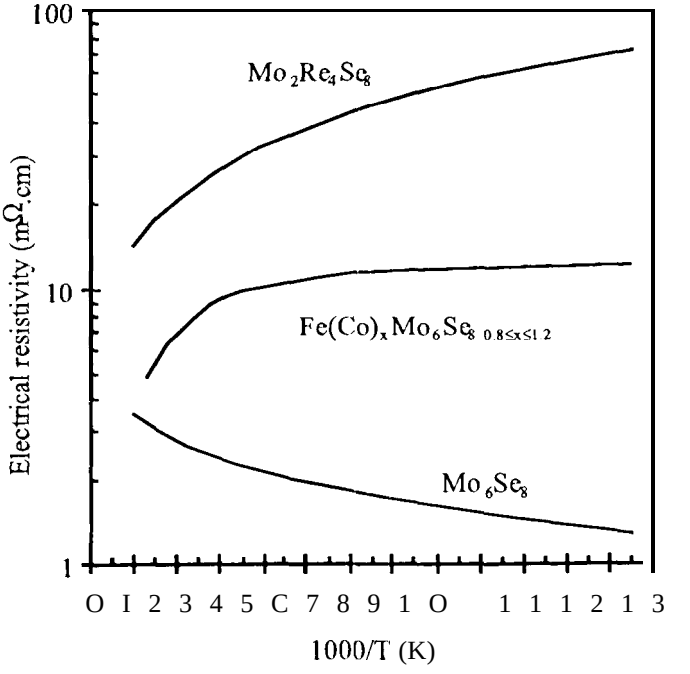

Figure 3: Electrical resistivity versus inverse temperature for Mo_6Se_8, $Mo_2Re_4Se_8$ and $(Fe,Co)_xMo_6Se_8$ Chevrel phases

The Seebeck coefficient and electrical resistivity for Mo_6Se_8 arc typical of a metal. For $Mo_2Re_4Se_8$ (with a VEC of 4), the conductivity is n-type , the Seebeck coefficient values are relatively large (up to -200 μV/K at 1100K) and the electrical resistivity decreases with increasing temperature. This clearly indicates a semiconducting behavior which is consistent with the VEC 'magic' number of 4. For $(Fe,Co)_xMo_6Se_8$ compositions, it was determined by MPA that the fraction, x, of Fc and Co in the samples was comprised between 0.8 and 1.2 presumably due to some material losses during the synthesis process, Therefore, the VEC for these compositions ranges between 3.6 and 3.7. For these samples, the Seebeck coefficient as well as the electrical resistivity are slightly increased compare to Mo_6Se_8 and the samples are semi-metallic. Again, this seems to be consistent with the VEC rule for these materials. The carrier concentration for these

filled compositions are about 2 x 10^{21} cm^{-3} and the carrier mobility is about 1 $cm^2 V^{-1} s^{-1}$.

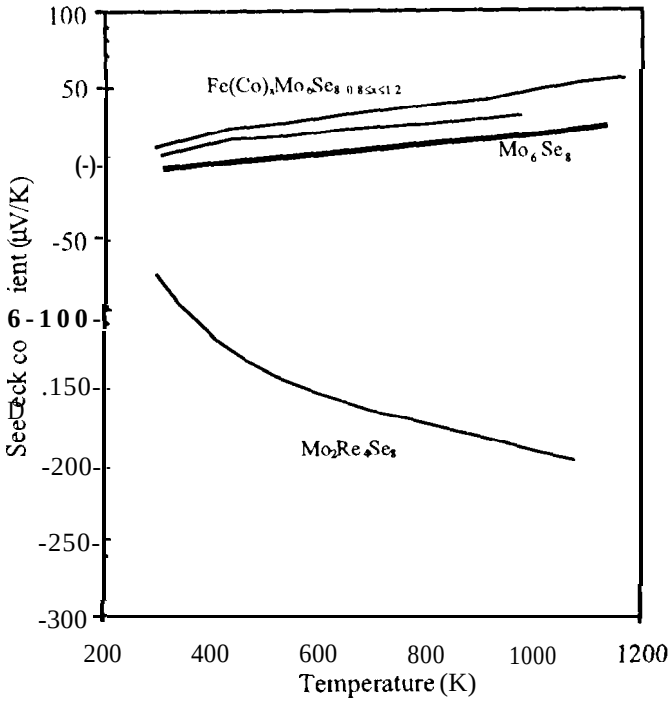

Figure 4: Seebeck coefficient versus temperature for Mo_6Se_8, $Mo_2Re_4Se_8$ and $(Fe,Co)_xMo_6Se_8$ Chevrel phases

The results of thermal conductivity measurements arc shown in Figure 5. The room temperature thermal conductivity for Mo_6Se_8 is about 70 mW/cmK and the thermal conductivity decreases with increasing temperature to a minimum value of about 45 mW/cmK at 1100K, For $Mo_2Re_4Se_8$, the thermal conductivity is significantly decreased with a room temperature thermal conductivity of 40 mW/cmK. Considering the relatively large electrical resistivity values, the total thermal conductivity shown corresponds to approximately 98% of the lattice contribution. The thermal conductivity varies approximately as $T^{-1/2}$ which is indicative of a dominant phonon scattering by point defects introduced by the substitution of Re for Mo atoms. A remarkable decrease in thermal conductivity is obtained for $(Fe,Co)_xMo_6Se_8$ compositions. The room temperature thermal conductivity is about 13 mW/cmK for these compositions and the thermal conductivity rises with increasing temperature as for glass-like materials, The lattice thermal conductivity values, calculated using the Wiedemann-Franz law assuming the Lorenz number to be 2.44 x 10^{-8} V^2/K^2, are represented by the dashed lines in Figure 5 for Mo_6Se_8 and $(Fe,Co)_xMo_6Se_8$ compositions. For the filled compositions, the lattice thermal conductivity increases from a room temperature value of 10 mW/cmK to 13 mW/cmK at 11 OOK. As wc pointed out above, these compositions are semi-metallic and one can expect a significant electrical carrier-phonon scattering which should lower the lattice thermal conductivity. However, it is known that this type of phonon scattering cannot lead to a glass-like behavior for the thermal conductivity and therefore the strong decrease in the thermal conductivity can predominantly be attributed to the "rattling" of the Co or Fe atoms in the voids of the Chevrel structure.

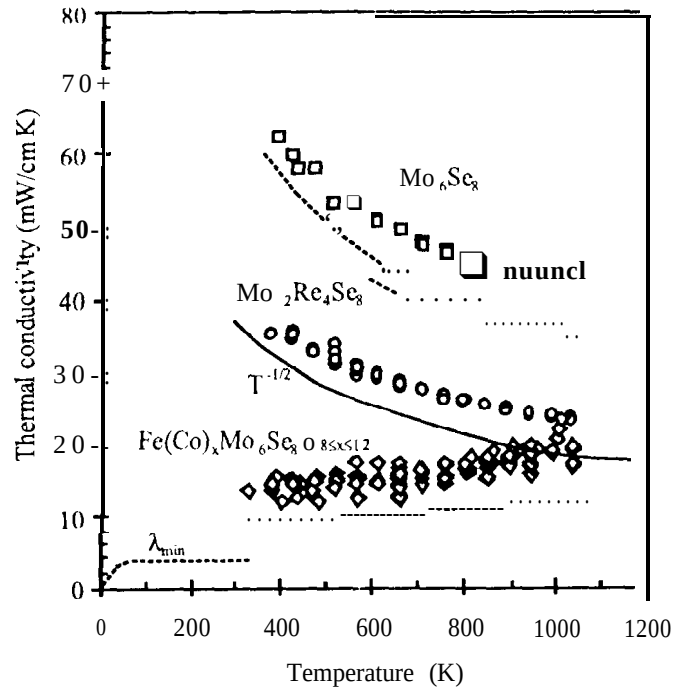

Figure 5: Seebeck coefficient versus temperature for Mo_6Se_8, $Mo_2Re_4Se_8$ and $(Fe,Co)_xMo_6Se_8$ Chevrel phases. The dashed lines represent the lattice thermal conductivity for Mo_6Se_8 and $(Fe,Co)_xMo_6Se_8$ compositions. The calculated minimum lattice thermal conductivity is also reported (see text for details of calculations).

It was interesting to compare the experimental values obtained for $(Fe,Co)_xMo_6Se_8$ compositions to the calculated minimum thermal conductivity, a concept first proposed by Slack [22] and later developed by Cahill et al. based on a model due to Einstein [9]. The minimum thermal conductivity is expressed as a sum of three Debye integrals by [9]:

$$\lambda_{min} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_i v_i \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{(e^x-1)^2} dx$$

The sum is taken over the three sound modes (two transverse and one longitudinal) with speeds of sound v_i. k_B is the Boltzmann's constant, n the atomic density, T the temperature in K and $\theta_i = v_i (h/2\pi k_B) (6\pi^2 n)^{1/3}$. Using the measured transverse and longitudinal of 1.52 x 10^3 ms and 2.63 x 10^3 ms^{-1}, respectively and an atomic density of 5.04 x 10^{28} m^{-3}, we calculated the minimum thermal conductivity values fOr $Fe_{1.2}Mo_6Se_8$. The results are reported in Figure 5. At room temperature, the calculated value is about 3 times the measured value, indicating that further reduction in thermal conductivity might be possible, The data reported for the filled compositions in Figure 5 correspond to materials which arc about 50% filled and future studies on Chevrel phases will investigate the impact of various degree of tilling on the thermal conductivity. In addition to the filling fraction, the effect of introducing various large atoms well as a combination of small and large atoms in the voids should be studied. In selecting Chevrel phases for further investigations,

one should obviously also pay attention to the VEC which should be close to 4 to achieve a semiconducting behavior. Preliminary data on the thermoelectric properties of Chevrel phases show that void fillers can be very effective in producing significant phonon scattering, resulting in relatively low lattice thermal conductivity values. The major questions which remain to be answered to fully assess the potential of thermoelectric applications are: 1) how low can the thermal conductivity be decreased ? and 2) can semiconducting Chevrel phases with good carrier mobility be obtained ?

Re_6Te_{15}

The structure of the cluster compound Re_6Te_{15} was studied in details by Klaiber et al. [23]. This compound, with 84 atoms per unit cell, belongs to the space group *Pbca* with a=13.003Å, b=12.935Å and c=14.212Å. The crystal structure presents some similarities with the Chevrel phases and the Re atoms are also arranged in octahedral [Re_6] clusters. The thermoelectric properties of this compound have been little studied but some Seebeck coefficient and electrical resistivity data can be found in the literature [23,24]. In general, the samples were characterized by high Seebeck coefficient values as well as high electrical resistivity values. To be best of our knowledge, there is no data on the thermal conductivity of this compound. The heavy atoms constituting the compound as well as the large number of atoms per unit cell could give low thermal conductivity. It was also found that up to 40% of the Te atoms can be replaced by Se atoms [23] and this offers further possibilities to achieve lower thermal conductivity than for the binary compound Re_6Te_{15} itself. For the reasons mentioned above as well as some others that will be discussed in the one of the following section, we have started the preparation and characterization of Re_6Te_{15}-based materials. Initial results of the synthesis and characterization of the thermoelectric properties of these materials is presented and discussed in the following sections.

Experimental

Single phase, polycrystalline samples of $Re_6Te_{15-x}Se_x$ were prepared by mixing and reacting stoichiometric amounts of rhenium (99.997%), tellurium (99.9997.) and selenium (99.999%) powders. The powders were first mixed in a plastic vial using a mixer before being loaded into a quartz ampoule which was evacuated and scaled. The ampoules were then heated at 773K for 10 days with one intermediate crushing. The samples were analyzed by x-ray diffractometry (XRD) to check that they were single phase. The powders were then hot-pressed in graphite dies into dense samples, 10 mm long and 6,35 mm in diameter. The hot-pressing was conducted at a pressure of about 20,000 psi and at a temperatures of 773 K for about 2 hours under argon atmosphere, The density of the samples was calculated from the measured weight and dimensions and was found to be about 97% of the theoretical density.

The samples were characterized using the same microstructure and measurements techniques dcscribcd in the experimental section for the Chevrel phases. All samples were found to be single phase by microprobe analysis. The transverse and Iongitudinal speed of sounds were measured to be 1.38 x 10^3 m s^{-1} and 2.35 x 10^3 m s^{-1}, respectively.

Results and discussion

The electrical resistivity and the Seebeck coefficient values are reported for Re_6Te_{15} and Re_6Se_2 z~Tc1275 in Figures 6 and 7, respectively. In general, the results are consistent with previous findings [23,24]: all samples showed p-type conductivity with large Seebeck coefficient values and large electrical resistivity values. The room temperature carrier mobility for Re_6Te_{15} was 4 cm^2 V^{-1} s^{-1} for a carrier concentrat ion of 2 x 10^{18} cm"'. The electrical resistivity are high, due to the low carrier mobility. For Re_6Te_{15}, both electrical resistivity and Seebeck coefficient decrease with increasing temperature, as expected for an intrinsic semiconductor. The electrical resistivity varies linearly with temperature at high temperatures. We calculated an activation energy of 0.8 eV, in good agreement with previous results [23]. A different behavior is observed for the Re&e2z~Te127s solid solution. Both Seebeck coefficient and electrical resistivity increase with increasing temperature and only at the highest temperatures of measurements, an onset of intrinsic behavior can be observed. However, the electrical resistivity are also relatively high which is due again to relatively poor carrier mobility of the order of 1-2 cm^2 V^{-1} S-*.

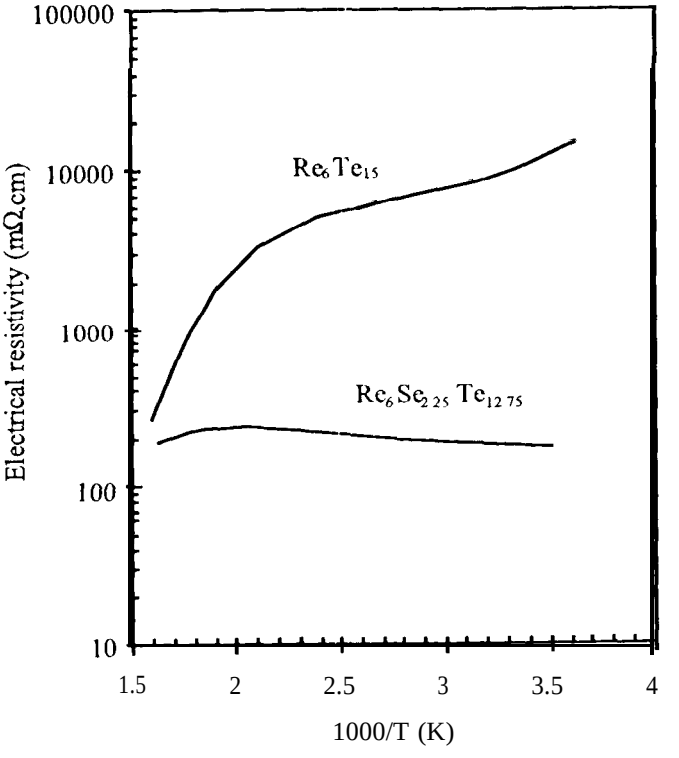

Figure 6: Electrical resistivity versus inverse temperature for Re_6Te_{15} and $Re_6Se_{2\,25}Te_{12\,75}$

The results of the thermal conductivity measurements for Re_6Te_{15} and $Re_6Se_{2\,25}Te_{12\,75}$ are shown in Figure 8 and compared to typical values obtained for p-type state-of-the-art thermoelectric materials. Considering the high electrical resistivity of the samples, the electronic component of the total thermal conductivity is negligible and the values shown in Figure 8 can be considered as being the contribution) from

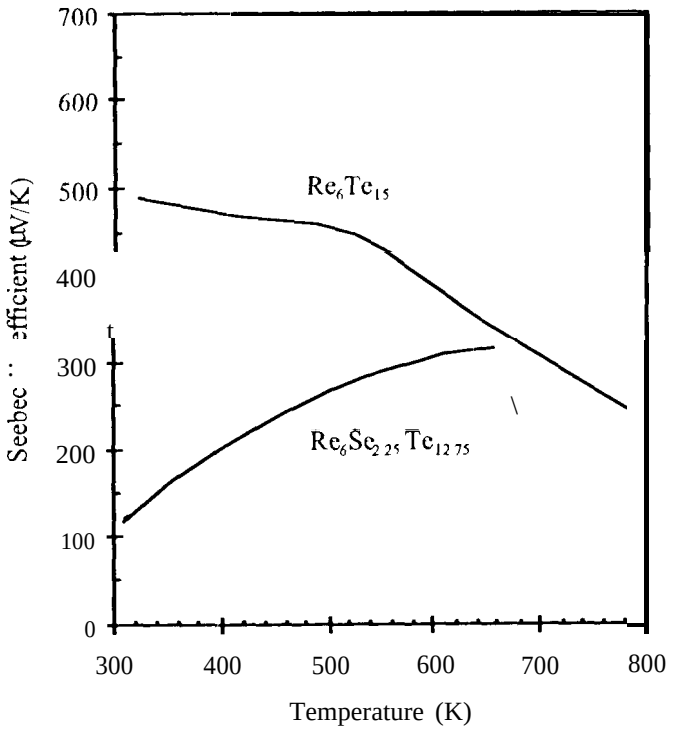

Figure 7: Seebeck coefficient versus temperature for Re_6Te_{15} and $Re_6Se_{2.25}Te_{12.75}$

the lattice only. At room temperature, the thermal conductivity for Re_6Te_{15} is about 14 mW/cmK and is comparable to p-type Bi_2Te_3-based alloys. The thermal conductivity of Re_6Te_{15} decreases with increasing temperature following reasonably well a 1/T dependence, as expected for phonon-phonon umklapp scattering. A minimum of 7 mW/cmK is reached at 800K, significantly lower than the values obtained for state-of-the-art thermoelectric materials. For the $Re_6Se_{2.25}Te_{12.75}$ solid solution, the thermal conductivity decreases with increasing temperature approximately as T^{-*n}. This temperature dependence is typical of a phonon scattering by point defects. The values for the solid solution are lower than for the binary compound because of the mass and volume fluctuations introduced by the substitution of Se atoms for Te atoms. At room temperature the thermal conductivity is 10 mW/cmK, decreasing to a minimum of 6 mW/cmK at 600K.

Using the same formalism presented above, we have calculated the minimum thermal conductivity y for Re_6Te_{15} which corresponds to the same material in the amorphous state. For the calculation, we used the measured speed of sounds and an atomic density of 3.52×10^{28} m^{-3}. The results are shown in Figure 8. At room temperature, the calculated minimum value is 2.3 mW/cmK and the minimum measured value is 10 mW/cmK for the $Re_6Se_{2.25}Te_{12.75}$ solid solution. This seems again to indicate that scattering of the phonons by point defects cannot yield thermal conductivity comparable to an amorphous material. As we mentioned earlier, the investigation of the thermoelectric properties of Re_6Te_{15} was primarily prompted by the possibility of achieving low thermal conductivity values because of the heavy masses of the elements forming the compounds as well as the large number of atoms per unit cell. The results show that indeed the thermal conductivity are low, significantly lower than for state-of-the-art thermoelectric materials between 300 and 800K. However, there also seems to be room for further reducing the lattice thermal conductivity. The second main reason which incited us to investigate the properties of Re_6Te_{15}-based materials is, as for the Chevrel phases, the presence of a number of voids in the structure. Figure 9 illustrates the location of the voids inside the crystal structure. The large spheres represent the atoms that can possibly be inserted in these voids. The radius of the voids is 2.754Å [23] and therefore each of the voids is large enough to accommodate a great number of different type atoms. 'Filled compositions can be represented by the formula $Re_6M_2Te_{15}$. Although the possibility of insetting additional atoms in the voids of the Re_6Te_{15} structure was suggested in the literature [23], this was not accomplished experimentally to the best of our knowledge

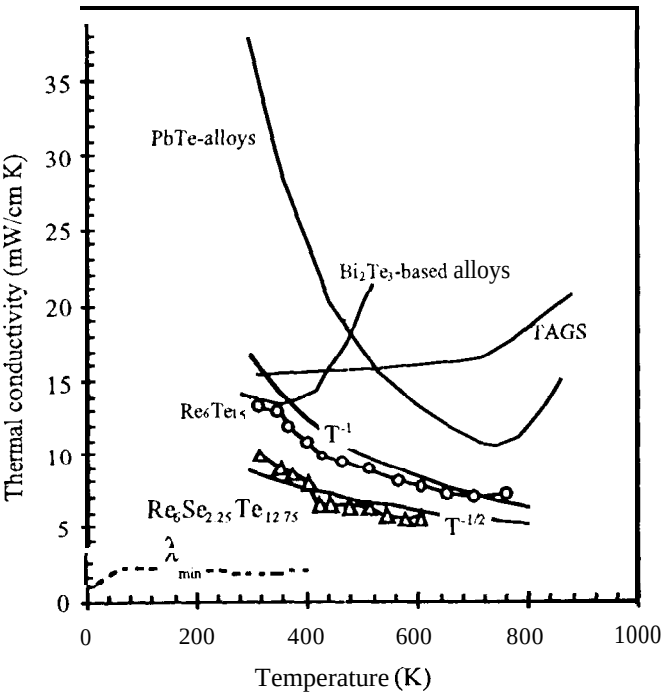

Figure 8: Thermal conductivity versus temperature for Re_6Te_{15} and $Re_6Se_{2.25}Te_{12.75}$. The calculated minimum lattice thermal conductivity is also reported (see text for details of calculations). The values for p-type stat c-of-the-art thermoelectric materials are also reported for comparison: Bi_2Te_3 and PbTc alloys and TAGS (Te-Ag-Ge-Sb alloys).

We have started the synthesis of filled Re_6Te_{15} samples with Ag, Cd and Fe. the tilling elements were added to the prc-synthesized Re_6Te_{15} powders and the mixtures were annealed for 5 days at 773K. The powders were then hot-pressed under the same conditions as unfilled Re_6Te_{15} samples. MPA of the samples filled with Fe and Cd showed a significant amount of secondary phases and no phase corresponding to a filled composition could be detected. For Ag filled samples, the samples were essentially composed of several filled compositions $Re_6Ag_xTe_{15}$ with $0.5 \le x \le 1.14$. This encouraging result suggests that it is indeed possible to till

the voids of the structure. The thermoelectric properties of the Ag filled sample are currently being 'investigated Improvements arc however needed to obtain homogeneous samples and also to ameliorate the synthesis technique and demonstrate the possibility of inserting other atoms in the voids. The study of the impact of the additional atoms on the thermal conductivity of these materials is of particular interest because it could result in very low thermal conductivity values, close to the theoretical minimum. Also, one can expect substantial modifications of the band structure of these materials and therefore different electrical properties.

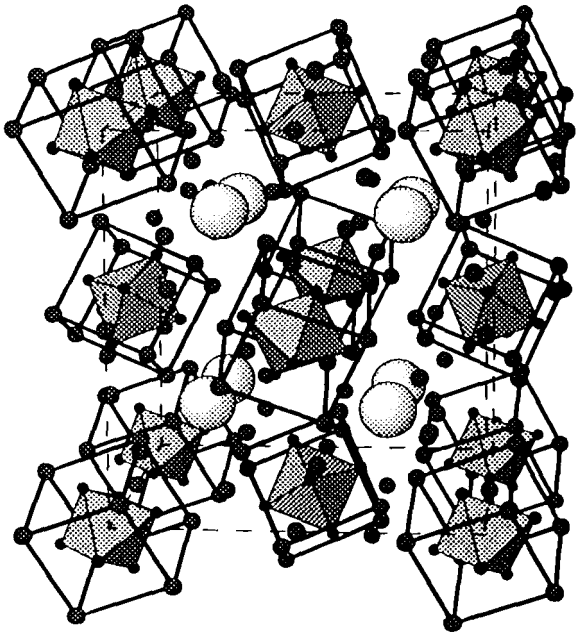

Figure 9: Illustration of the Re_6Te_{15} unit cell showing the $[Re_6]$ cluster surrounded by eight Te atoms. Large spheres representing atoms are inserted in the voids presented in the structure. Some Te atoms were omitted for clarity.

Conclusion

As part of an ongoing search for thermoelectric materials with superior thermoelectric properties, wc have started to investigate the properties of two classes of cluster compounds: Chevrel phases and ReGTclj-based materials. A common property of these materials is the presence of voids in their crystal structure which can be tilled with a variety of atoms. For the Chevrel phases, initial results showed that low thermal conductivity (~10 mW/cmK at 300K) can be achieved for filled compositions and even lower values might be possible by adjusting the nature of the filling element and its concentration. Wc have also shown that semiconducting Chevrel phases can be created by controlling the number of valence electrons, Semiconducting properties are observed for VEC of4. Some of the compositions prepared showed good Seebeck coefficient values but also poor carrier mobility which will need to be improved to achieve good thermoelectric figures of merit. $Rc_{fi}Tc_{i-}$-based materials showed very low thermal conductivity in the 300-800K temperature range (6-13 mW/cmK), large Seebeck coefficient but also poor carrier mobility. The possibility of introducing Ag atoms in their voids of the structure was also demonstrated and such filled compositions should possess very low thermal conductivity, close to the theoretical minimum The thermoelectric properties of Ag-filled compositions arc currently being investigated as well as the synthesis of other filled compositions. In summary, wc believe that these two new classes of materials offer a good potential for thermoelectric applications, including numerous possibilities for optimizing their properties. The concept of using loosely bound atoms in the crystal structure to obtain low thermal conductivity was demonstrated for the Chevrel phases,

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